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THE ETHERATES OF MAGNESIUM HALIDES

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THE ETHERATES OF MAGNESIUM HALIDES

CHAPTER I

HISTORICAL BACKGROUND AND PRESENTATION OF PROBLEM

Menschutkin (1) was the first to make a study of the solubilities of magnesium halides in diethyl ether. He studied the solubilities of magnesium bromide and magnesium iodide in diethyl ether over a wide range of temperatures. Menschutkin discovered that as the ether solutions of these halides became more concentrated, a heavy, oily, immiscible layer separated. When this oily layer was cooled, crystals separated. He found these crystals to be compounds of magnesium halide and ether. The term "etherate" was used by him in referring to these compounds. The formulas for these etherates were determined by Menschutkin to be 2 moles of ether for each mole of magnesium halide.

Other investigators have continued the study of ether solutions of magnesium halides. Ahrens and Stapler (2) have also reported that magnesium bromide and magnesium iodide each crystallize from anhydrous ether together with 2 moles of solvent. Domanitskii (3) recorded the existence of the monoetherate of magnesium chloride.

Meisenheimer and his co-workers (4,5,6) have also reported that when magnesium bromide and magnesium iodide were formed in ether solution, an oily, immiscible layer was formed. Meisenheimer, too, obtained etherate crystals of magnesium bromide and magnesium iodide upon cooling the heavy immiscible layer. According to him these etherate crystals contained 2 moles of ether for each mole of magnesium halide. Meisenheimer cited the insolubility of magnesium chloride in ethyl ether.

Noller (7) has reported the solubility of anhydrous magnesium chloride to be 0.001 mole of magnesium chloride per 1000 grams of ether.

Stewart and Ubbelohde (8) give accounts of the preparation of magnesium iodide under ether, and of the determination of the solubility of the dietherate of magnesium iodide in ether between the temperatures 0°C and 20°C. Menschutkin (1), Meisenheimer (4,5,6) and Stewart (8) have each described some of the properties of the etherates of magnesium bromide and magnesium iodide.

Many other researchers (9, 10, 11, 12, 13, 14) have made use of ether solutions of magnesium halides and indicate the existence of etherates of these salts. In many of these cases, however, it would be concluded from reading the reports of their work that they assumed the etherate used had one or more molecules of ether in combination with the magnesium halide.

Rowley (15, 16, 17) reported that magnesium bromide formed not one but several etherates. By conducting vapor pressure measurements of ether solutions of magnesium bromide and by determining the solubility of magnesium bromide in ether, he found evidence to support the conclusion that there was a trietherate which was stable to about 12.5°C, a dietherate stable from this temperature to approximately 22.5°C. At this temperature the crystals melted under ether to form two conjugate liquid phases. The existence of several etherates had not been indicated in previous accounts of the preparation of these compounds.

A review of the reported solubilities of magnesium bromide and magnesium iodide in ether (1, 8, 17) shows that magnesium iodide is much more soluble in ether than is magnesium bromide. From the periodic relationship of bromine and iodine this difference in solubility is to be expected (18). In addition, since magnesium bromide has been shown to form a series of etherates, we would expect magnesium iodide to exhibit a similar behavior. The greater solubility of magnesium iodide over magnesium bromide suggests that perhaps magnesium iodide would form etherates more readily than magnesium bromide. The presence of more than one etherate of magnesium iodide has not been reported heretofore.

The purpose of this research was threefold. First, an investigation was undertaken that would lead to the identification of a series of etherates of magnesium iodide, should they exist. Second, since it had been indicated previously (6, 7) that magnesium chloride is quite insoluble in ethyl ether and also (3, 10) that it forms the monoetherate, an investigation of the solubility of magnesium chloride was carried out. Third, since there is no mention in the literature of the solubility of magnesium fluoride in ethyl ether, it is desirable, in order to get a more complete picture of the magnesium halides, to investigate the solubility of magnesium fluoride in ether.

The general pattern of research was as follows. First, the anhydrous halides were prepared. Second, their solubilities in ethyl ether were determined between 0°C and and 30°C. Third, the solid phases in equilibrium with the liquid phase were analyzed to determine their composition. Fourth, from the fundamental relationship

$$\frac{d\ln S}{dT} = \frac{\Delta H}{RT^2}$$

where H is the molar heat of solution, T the absolute temperature at which the solubility was measured and R the gas constant, evidence for etherate formation was obtained. The logarithm of the solubility was plotted against the reciprocal of the absolute temperature. If it is assumed that the heat of solution remains constant over the temperature range used, such a plotting should give a straight line as long as the phase in equilibrium with the solution does not change.

CHAPTER II

EXPERIMENTAL ANALYSES AND MATERIALS

Methods of Analysis

In the performance of the experimental work it was necessary to analyze for the following ions: fluoride, chloride, bromide, iodide, and magnesium. The methods used were the standard ones, but there were some special considerations that needed to be given to some of the particular situations under which the analysis was to be made.

Analysis for fluoride. The fluoride content was determined by the method of Willard and Winter as modified by Rowley and Churchill (19, 22). The solid material was distilled with steam in the presence of sulfuric acid and excess silica. The collected distillate was then titrated with standard thorium nitrate solution.

Analysis for chloride, bromide and iodide. Chloride, bromide and iodide contents were determined by the Volhard method (20). In the case of the chloride the modification developed by Caldwell (21) was employed. It was found that the reaction between water and the magnesium halide was vigorous enough to result in a loss of hydrogen halide. To lessen this, the sample was first dissolved in about 10 milliliters of 95 per cent ethyl alcohol. If both magnesium and halide were to be determined on the same sample, the solution was made up to 100 milliliters and an aliquot used for the analysis. Otherwise, the sample was diluted to about 50 milliliters with water and the titration performed directly.

Analysis for magnesium. The magnesium content was determined by weighing as magnesium sulfate (23). The sample was transferred to a tared crucible. Concentrated sulfuric acid was added and the excess acid was removed by heating the crucible on a hot plate. The resulting magnesium salt was heated to redness and weighed as magnesium sulfate. This method of determining magnesium is suitable since there are no interferring ions present.

A modification of this procedure was made when both halide and magnesium were to be determined on the same sample and from the same solution. Before the solution was diluted to 100 milliliters, 40 milliliters of diluted sulfuric acid (1:3) was added. This was necessary to prevent the hydrolysis of the magnesium halide. An aliquot of this solution was then transferred to the weighed crucible and evaporated. This procedure was applicable to magnesium chloride and magnesium bromide. When magnesium iodide was to be determined, free iodine was liberated. Because of this, magnesium and iodide were determined on separate samples.

The results of the analyses were reported in terms of magnesium fluoride, magnesium chloride, magnesium bromide and magnesium iodide.

Preparation of Anhydrous Magnesium Halides

Materials Used

Ethyl ether. Absolute ether (Merck) was used. As an added precaution against the presence of water, pieces of freshly cut sodium were added and the ether kept in a closet for two or three days. It was then filtered onto fresh sodium and distilled onto fresh sodium. The ether was stored in a closet in a brown bottle until it was to be used. Only the middle portion of the distilled ether was taken for use and the ether was freshly distilled if the storage period was extended over a period of a week.

Inorganic chemicals. In the preparation of magnesium iodide and magnesium bromide Grignard quality magnesium (Merck) was utilized. The iodine was of C. P. quality and sublimed before use. Reagent mercuric bromide (Baker) and reagent mercuric iodide (Baker) were used. Both of these reagents were further purified by sublimation before they were employed in a reaction.

Reagent magnesium chloride hexahydrate (Baker) and reagent ammonium chloride (Baker) were used without additional purification in the preparation of magnesium chloride.

Analytical reagent grade hydrofluoric acid (Mallinckrodt) and reagent magnesium carbonate (Mallinckrodt) were used as purchased for the preparation of magnesium fluoride.

Preparation of Anhydrous Magnesium Fluoride

The method selected to prepare magnesium fluoride was to react hydrofluoric acid with magnesium carbonate. A survey of the literature (24, 25, 26) indicates that a filterable magnesium fluoride can be prepared in this manner and that the product can be dried and ignited without alteration.

In a typical preparation, 30 grams of magnesium carbonate were weighed into a platinum dish. Sufficient hydrofluoric acid was added dropwise to decompose the carbonate and then about 5 milliliters in excess were added. The mixture was stirred with a stiff platinum wire. After the reaction mixture had ceased to effervesce, the dish was placed on a hot plate and the water and excess hydrofluoric acid were evaporated slowly, the mixture being stirred frequently. When the mixture had reached the consistency of a thick paste, another 5 milliliters of hydrofluoric acid were stirred into the paste. This mixture was evaporated to dryness and the dried material was crushed fine. Another 5 milliliters of hydrofluoric acid were added, the mixture was stirred, taken to dryness and crushed to a powder.

A sample of this dried material was weighed into a tared platinum crucible and the magnesium content determined. Another portion was weighed into the distilling flask of the fluoride distillation apparatus. The fluoride was distilled and the amount determined by titration with thorium nitrate. The results of these analyses were calculated as magnesium fluoride. Analyses which are indicative of the results obtained are shown in Table 1.

Ignition of magnesium fluoride. The analysis results show that the fluoride content of the sample so prepared was in excess of the amount to be expected in magnesium fluoride. This could be explained by considering that the hydrofluoric acid had not been completely removed, which could be expected under the conditions of the preparation.

A portion of the material that had been taken to dryness on the hot plate was placed in a platinum crucible and set in the drying oven at 110°C. Drying at this temperature was continued for a period of about 48 hours. During this heating the material constantly lost weight. After the 48 hour drying period, fluoride and magnesium determinations were made. Representative results are shown in Table 1.

Some of the material that had been heated in the drying oven at 110°C was ignited to red heat in an open crucible. Weight was gradually lost until the final weight was about 60 per cent of the original. Fluoride and magnesium analyses were made. In Table 1 are shown results which indicate what happened upon ignition of the magnesium fluoride.

TABLE 1

ANALYSIS OF MAGNESIUM FLUORIDE AT VARIOUS STAGES IN ITS PREPARATION

Treatment	% MgF_2 from Mg analysis	% MgF_2 from F analysis
Taken just to dryness on hot plate	94 %	107 %
After heating at 110°	77 %	94 %
After heating to red heat	57 %	0 %

The data in Table 1 indicates that heating magnesium fluoride results in changes in the magnesium fluoride.

Effect of air upon ignition. In an effort to find out more about the effect of ignition upon magnesium fluoride, a brief study of the influence of air was made. A quantity of magnesium fluoride, that had been taken just to dryness on the hot plate, was divided into three portions. Portion 1 was ignited for 2 intervals of 30 minutes each in an open crucible. Portion 2 was ignited in a covered crucible. Portion 3 was ignited in an atmosphere of nitrogen. The results of these ignitions are shown in Table 2.

TABLE 2

LOSS IN WEIGHT OF MAGNESIUM FLUORIDE UPON IGNITION

Sample	after 30 minutes	after 60 minutes
Portion 1	14 %	20 %
Portion 2	9 %	11 %
Portion 3	8 %	9 %

The results of Table 2 indicate that magnesium fluoride cannot be heated in air without changes taking place.

It is apparent that more should be done with this reaction. However, it was thought that the material that was prepared on the hot plate was of sufficient purity to give an indication as to the solubility of magnesium fluoride. The presence of a small excess of hydrofluoric acid should introduce no great error.

Preparation of Magnesium Chloride

Anhydrous magnesium chloride was prepared by heating magnesium chloride hexahydrate and ammonium chloride in a molar ratio of 1:3 (7, 27). A representative preparation was to use 20 grams of magnesium chloride hexahydrate and 16 grams of ammonium chloride. This mixture was ground together. Then it was transferred to an upright combustion tube, which was about 8 inches long and equipped with an exit tube at right angles to the main body of the tube. The mixture was heated slowly to drive off the excess water. After this excess water was driven off, more heat was applied to decompose the ammonium chloride. The solid material was then fused.

When cool, the end of the tube was broken under an atmosphere of nitrogen. The chunks of magnesium chloride were then broken up, still under dry nitrogen, and the material transferred to a weighing bottle. This bottle and contents were kept in a desiccator over concentrated sulfuric acid.

The purity of the magnesium chloride thus prepared was determined on the basis of both the chloride and magnesium content. These analyses showed the purity to be 99 per cent magnesium chloride as calculated from the chloride content and 103 per cent as calculated from the magnesium content. This analysis does indicate the presence of a very small amount of magnesium oxide. However, it is believed that the purity is satisfactory for the use intended.

Preparation of Magnesium Iodide by Direct Combination

For most of the experiments described in Chapter 1, magnesium iodide was prepared by reacting iodine with magnesium under ether (1, 8, 9, 12, 28). Meisenheimer (4) and

Stewart (8), among others, had reported upon the instability of the prepared ether solution of magnesium iodide, particularly upon contact with air and upon exposure to strong light. According to them, the etherate became yellowish-brown after several hours and brown after a day.

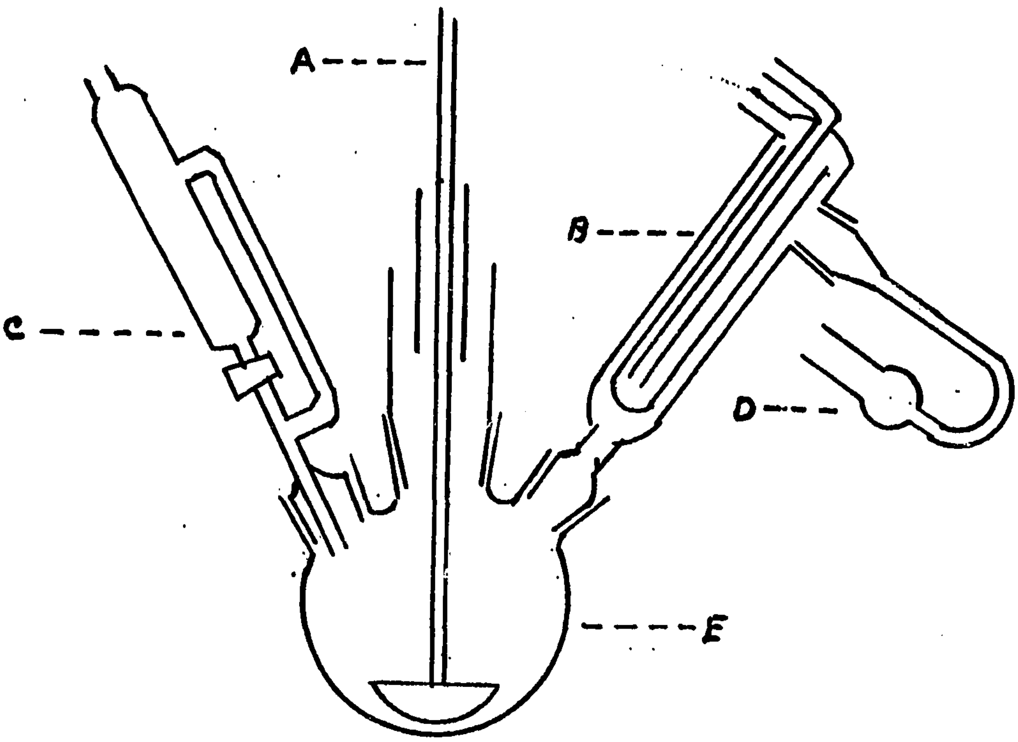
In the present work it was desirable to have a product that was as stable as possible, since the presence of the decomposition products would alter the results of solubility measurements. As the first approach to the problem it was decided to prepare magnesium iodide from magnesium and iodine under ether and then to determine whether or not the product thus prepared was sufficiently stable to warrant its use in this experiment. It was recognized that others had made solubility measurements of magnesium iodide as prepared in this manner. It was also thought that if the stability could be improved there might be some variation in the solubility results obtained.

Pyrex glassware with standard taper ground glass connections was used throughout. Before being assembled the glassware was oven dried at 110°C for at least 8 hours. All joints were lubricated with silicone lubricant, and all openings were protected with calcium chloride drying tubes. Whenever heat was needed to further the reaction, a Glascol mantle heater was employed.

In a representative preparation 13 grams of magnesium were placed in the reaction flask. The apparatus was then assembled as shown in Figure 1. The system was then flushed with dry nitrogen for one hour, during which time the flask was warmed to about 100°C. At the conclusion of this drying period the system was allowed to cool to room temperature, nitrogen still being passed through the system. Enough ether was added to cover the magnesium. Thirty grams of iodine were dissolved in 100 milliliters of ether and this solution placed in the dropping funnel. The iodine-ether solution was added slowly to the reaction flask, the rate of addition being regulated so that the ether refluxed gently.

When about one-half of the iodine had been added the heavy, oily, immiscible layer was observed. After all of the iodine-ether mixture had been added and the reaction rate had subsided, the flask was warmed so that the ether refluxed slowly. This refluxing was continued until the brown solution changed to a colorless one. Usually about six hours were required to reach this stage. During the refluxing period fresh ether was added to replace any lost during the process.

The ether solution of magnesium iodide was then transferred to a dry graduate. To accomplish this, a bent adapter with a ground glass connection was fitted with a glass wool plug and oven dried at 110°C. A 100 milliliter graduate was also oven dried. The graduate and adapter, after cooling to room temperature, were rinsed with dry ether. The adapter was substituted for the dropping funnel



A ... Motor driven stirrer, mercury sealed

B .... Friedrich reflux condenser

C .... Pressure equalizing dropping funnel

D .... Calcium chloride drying tube

E .... Reaction flask

Apparatus Used to Prepare Magnesium Iodide

FIGURE 1

in the reaction flask. The ether solution was decanted through the adapter into the graduate. This transfer was made in an atmosphere of dry nitrogen. The graduate was fitted with a calcium chloride drying tube and placed in a cold bath at $0^{o}C$. Nearly white needle-like crystals separated in the graduate.

Stability of magnesium iodide as prepared by direct combination. Samples of the crystals were removed from the graduate and placed in 2 separate weighing bottles. The bottles were then placed in separate desiccator jars. These desiccators served merely as containers. One of the desiccators was placed in a desk cupboard and the other one was placed on top of the desk. After 24 hours these two samples were compared. Both had turned brown. The crystals placed on the desk top had become darker than the ones stored in the dark cupboard. During this same period the crystals that had remained in contact with ether in the bath at $0^{o}C$ had turned yellow-brown.

On several occasions after magnesium iodide had been prepared, as described above, and the crystals formed by cooling, it was observed that as the crystals aged, considerable amount of black or dark brown oily material was present throughout the mass of crystals. This black material was soluble in benzene. On occasion it was found to be difficult to make a transfer of the ether double layer and not have the ether solution almost immediately turn yellow.

In most cases of preparing magnesium iodide in this manner, the ether solution had an acrid odor. No attempt was made to determine the nature of these impurities. Rowley (16, 32) discusses the nature of the products when bromine reacts with ether. It was felt that if a method of preparation could be found which would result in fewer side reactions that it would be possible to prepare an ether solution of magnesium iodide which would be stable for a longer period of time and perhaps be more suitable to the demands of this series of experiments. Rowley (16) had shown this to be the case in the preparation of magnesium bromide from the elements.

Preparation of Magnesium Iodide by Displacement

Gomberg and Backman (29, 30) had made use of displacement reactions to prepare magnesium bromide and magnesium iodide. Rheinboldt and Schwenzen (31) had also reported that inorganic halides could be reduced by magnesium in ether. This method of preparation presented some advantages as it would not involve the presence of free iodine.

The apparatus as illustrated in Figure 1 was used. Thirteen grams of magnesium and 40 grams of mercuric iodide were placed in the reaction flask. The system was dried by passing dry nitrogen through it for one hour, during which period the reaction flask was warmed slightly. After this drying period the system was allowed to cool to room temperature. One hundred milliliters of ether was added through the dropping funnel. After a brief induction period the mixture underwent a vigorous reaction. During this induction period the ether became turbid, but the solution cleared as the reaction proceeded.

When the reaction had subsided, sufficient heat was applied to gently reflux the ether. This refluxing was continued for about 6 hours. Additional ether was added to replace any lost during the reaction. The oily, immiscible layer was in evidence. The mixture was allowed to cool to room temperature. The ether double layer was decanted through a glass wool plug, under nitrogen, into a 100 milliliter graduate which had been oven dried and rinsed with ether.

The graduate was equipped with a calcium chloride drying tube and placed in a bath at 0°C. White needle-like crystals separated.

Comparison of the two methods of preparing magnesium iodide. There is a definite advantage in preparing magnesium iodide by the displacement method. In the first place the etherate crystals are whiter. The color of the ether solution did turn yellow after 48 hours. However, the color was not only lighter, but was slower in forming, thus giving evidence that the etherate was more stable. There was no evidence of a dark brown oily material in contact with aged crystals of magnesium iodide etherate crystals, as was the case when prepared from the elements.

A qualitative test for mercury showed that no mercury was present in the ether solution so prepared.

Several tests showed that the ether solution prepared by displacement could be preserved a longer period of time with less decomposition. Still, light did affect the material. Some of the magnesium iodide-ether solution was stored in graduates of actinic glass. It was found that these solutions stored in actinic glass could be kept for several weeks with only a pale yellow coloration developing.

It was decided to prepare the ether solution of magnesium iodide by reacting magnesium with mercuric iodide under ether and to store the preparation in actinic glass graduates.

Preparation of Magnesium Bromide by Displacement

Rowley (15, 16, 17, 32) had prepared magnesium bromide by reacting magnesium with bromine under ether. He has determined the solubility of this magnesium bromide. In the previous section it was indicated that the magnesium iodide to be used for solubility measurements was prepared by a displacement reaction. It was decided to prepare magnesium bromide by a similar method and check the solubility results with those of Rowley. Rowley had suggested that bromine reacted with ether to produce products of side reactions which might affect the solubility of magnesium bromide.

The same apparatus and technique as used for the preparation of magnesium iodide were employed. Ten grams of magnesium and 25 grams of mercuric bromide were used. The reaction proceeded more vigorously than in the case of the magnesium and mercuric iodide. Water white double layers were produced. These were decanted into a dried graduate. The graduate, equipped with a calcium chloride drying tube, was then placed in a refrigerator bath at 0°C. White crystals were formed. These crystals were slow in forming, and in most cases some agitation was necessary. In the case of magnesium iodide etherate, the crystals formed immediately and easily.

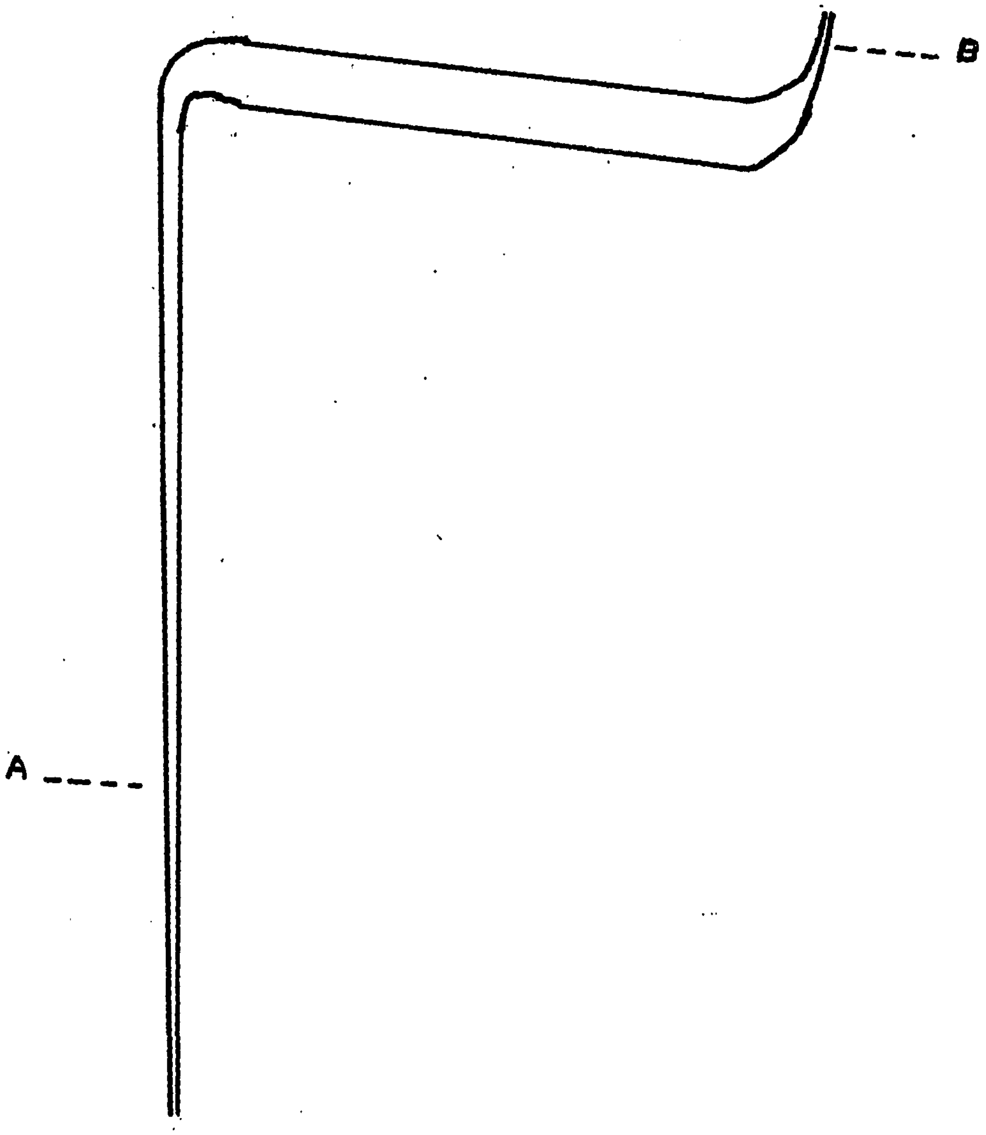
CHAPTER III

EXPERIMENTAL PROCEDURES

Sampling Procedure

It was necessary to develop a method of sampling the ether solutions. Obtaining a sample of ether presented a problem because of its volatility. It has been established that the etherates of magnesium bromide and magnesium iodide are decomposed by contact with air and moisture. Rowley (16) has shown that the introduction of moisture after preparation will increase the solubility of magnesium bromide in ether. He (33) has also made a study of the three phase system, water-ether-magnesium bromide.

A pipette similar to that shown in Figure 2 was made from 8 millimeter soft glass tubing. The bulb was about three inches long and the tip A about 8-10 inches long. The tip B was sealed. Before taking a sample the pipette bulb was warmed and ether drawn up into it. This would occur when the bulb was cooled by wrapping it with gauze saturated with chloroform. The ether was then forced out by heating the bulb, the pipette was cooled to room temperature and weighed. The bulb was again warmed and the tip A



Sampling Pipette

FIGURE 2

quickly immersed into the ether solution. As the bulb cooled, the ether solution was drawn into the bulb. The pipette was withdrawn when the bulb was about three-fourths full. Cooling of the bulb reduced the volatility of the ether so that the tip could be drawn out and sealed with the aid of a small flame. The pipette and pieces of the tip were reweighed.

The sample was transferred to a 250 milliliter erlynmeyer flask containing about 10 milliliters of 95 per cent ethyl alcohol. The tip was broken under the surface of the liquid by tapping against the bottom of the flask. The warmth of the hand was sufficient to force nearly all of the solution out of the bulb. The bulb was rinsed by breaking tip B and forcing water through the pipette.

This method of sampling was employed in determining the solubilities of magnesium bromide and magnesium iodide because the ether solution could be transferred without contact with the air.

Solubility of Magnesium Iodide

As was mentioned in Chapter II, crystals of magnesium iodide etherate were formed by cooling the double layer mixture. White needle-like crystals had formed. In preparing for solubility measurements the supernatant ether was decanted from the crystals and the graduate was filled with fresh ether. The graduate of actinic glass was fitted with a two hole stopper; one hole was plugged and a calcium chloride drying tube was fitted into the other.

The graduate was clamped into position in a constant temperature bath. For this purpose a Sargent Constant Temperature Bath (S-84805) was used. The temperature of the bath was set at 31°C. At this temperature the crystals dissolved and the oily, immiscible lower layer was formed. The graduate was shaken by swirling at frequent intervals until the two layers came to equilibrium. This point was indicated by a series of analyses of the upper layer.

The temperature of the bath was lowered slowly to 30°C. During this period the graduate was shaken frequently. A period of about five hours was allowed for equilibrium to be reached. Analysis of the upper layer was taken at this temperature. The analysis of this upper layer was repeated at temperature intervals down to 0°C. During each resetting of the temperature the graduate was shaken frequently and at least a five hour time interval was allowed.

At bath temperatures below room temperature, coolant from a refrigerated bath was pumped through the cooling coils of the constant temperature bath. For 0°C an ice-water mixture was employed and the several readings below 0°C were taken in the refrigerated bath itself.

As the temperature of the bath was lowered from 31°C there was a change in the saturating phase. The saturating phase that was present at first was the heavy, oily, immiscible lower layer. As the temperature was lowered this heavy layer was replaced by solid crystals.

All solubilities were calculated as grams of magnesium iodide per 100 grams of ethyl ether and the results are given in Table 3 in Chapter IV.

Some solubility measurements were made on the heavy oily layer. Representative measurements are given in Table 4 in Chapter IV.

Analysis of solid phase. After the crystals of magnesium iodide etherate had formed they were analyzed for magnesium and iodide. The per cent magnesium iodide was then calculated and the per cent ether determined by difference. These analyses were performed at several temperatures suggested by the graphs when the data of Table 3 were plotted. This information was used in conjunction with the graphs to indicate the phase changes taking place. The results of the analysis of the solid phase are given in Table 5 in Chapter IV.

These crystals were obtained for analysis by removing them from the graduate with a flat spoon prepared from a nickel spatula. They were allowed to drain and the excess ether then quickly blotted off with the aid of filter paper. This was done in an atmosphere of dry nitrogen. These crystals were transferred to a weighing bottle and quickly weighed. The crystals were analyzed by methods described in Chapter II.

Stability during solubility tests. Under the conditions of the experimental work, at the end of a series of analyses from 30°C to 0°C, practically no decomposition of magnesium iodide was indicated. The ether layer was only a pale yellow color and the crystals of etherate were still white in color. This was true even though the analysis period at times extended over a period of at least a week.

As another check on the purity of the product, determinations of magnesium and iodide were made at intervals on the same sample. As long as a ratio Mg:I::1:2 was maintained, it was assumed that decomposition had not taken place. In general the solubility of magnesium iodide was determined by the determination of only the iodide in solution.

Solubility of Magnesium Bromide

The techniques employed and the procedure followed in determining the solubility of magnesium bromide were the same as those described above for magnesium iodide. These results are given in Table 7 in Chapter IV.

Solubility of Magnesium Fluoride

As was discussed in Chapter II, a pure sample of magnesium fluoride was not prepared. However, as described there, the material selected for solubility measurements was that material resulting from the taking to dryness on the hot plate of the mixture of magnesium carbonate and hydrofluoric acid.

A 150 milliliter round bottom flask was used to determine the solubility of magnesium fluoride in ether. This solubility flask was oven dried at 110°C and rinsed with ether. Approximately 5 grams of magnesium fluoride were placed in the flask and 100 milliliters of dry ether were added. A calcium chloride tube was inserted in the stopper. The solubility flask was then clamped in the constant temperature bath which had been set at 30°C. The flask was shaken at frequent intervals and after about 6 hours measurements were made.

Ten milliliters of the ether solution were transferred to a tared weighing bottle. The ether was first evaporated on a steam bath and finished on a low temperature hot plate. The weighing bottle was cooled and reweighed. The increase in weight was taken as the amount of magnesium fluoride dissolved.

Solubility of Magnesium Chloride

The technique used and the procedure followed in determining the solubility of magnesium chloride were the same as those used in determining the solubility of magnesium fluoride.

CHAPTER IV

EXPERIMENTAL RESULTS

Magnesium Iodide

The results obtained in the experimental procedures described in the previous chapters are tabulated in this chapter for convenient examination.

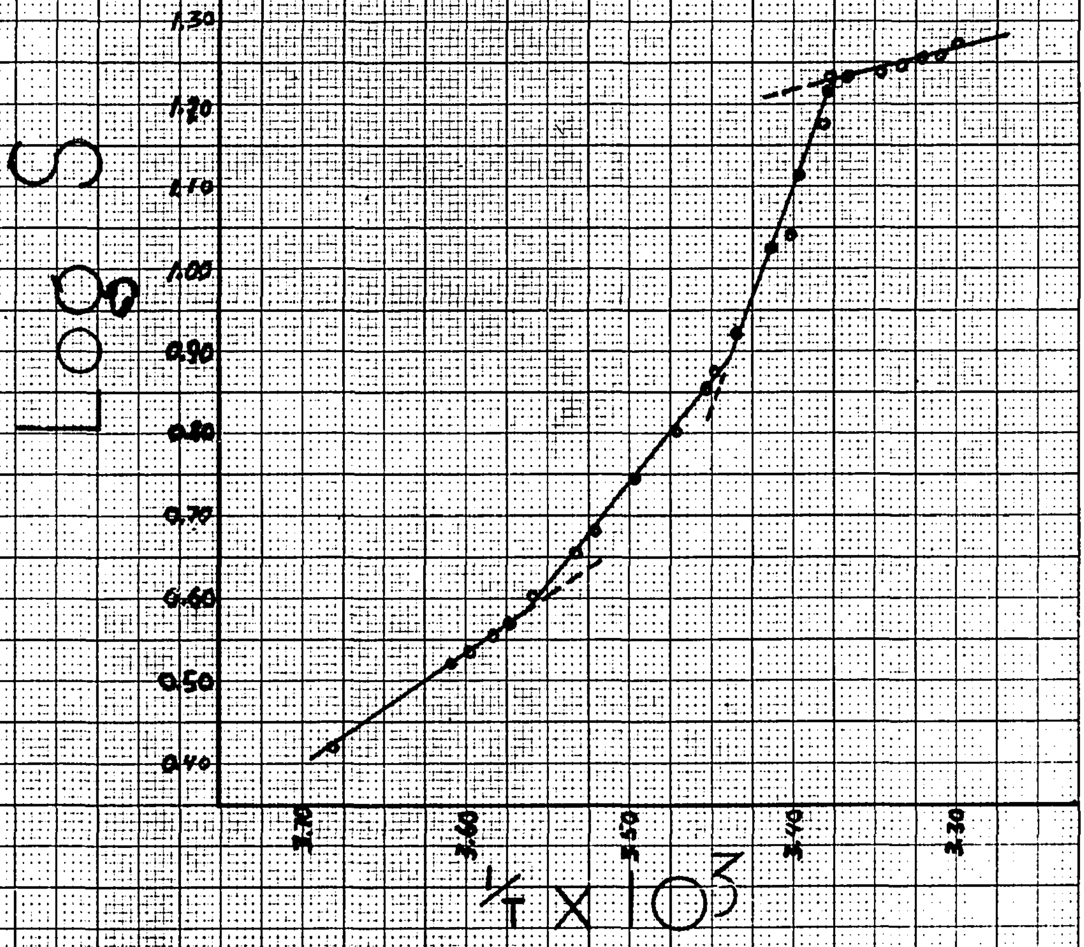
The data given in Table 3 are plotted to make the curve shown in Figure 3. In constructing this curve the logarithm of the solubility is plotted against the reciprocal of the absolute temperature.

Several samples of the solid phase were analyzed for magnesium iodide and the moles of ether in combination with one mole of magnesium iodide were then calculated. A summary of these analyses is given in Table 5.

TABLE 3

SOLUBILITY OF MAGNESIUM IODIDE IN ETHER

Temperature °C	Solubility $gMgI_2/100gEt_2O$	Temperature °C	Solubility $gMgI_2/100gEt_2O$
Equilibrium phase	Solid	20.0	10.6
-1.5	2.65	21.0	11.1
4.0	3.31	21.5	13.0
5.0	3.45	22.8	15.0
6.0	3.59	Equilibrium phase	immiscible layer
6.8	3.73	23.0	16.4
8.0	4.02	23.1	17.2
10.0	4.53	23.5	17.0
11.0	4.80	24.0	17.1
13.0	5.55	26.0	17.4
15.0	6.35	27.0	17.8
16.5	7.13	28.0	18.1
17.0	7.57	29.0	18.2
18.0	8.38	30.0	18.8



Graph of Solubility of Magnesium Iodide

FIGURE 3

TABLE 4

ANALYSIS OF LOWER OILY LAYER

Temperature °C	Solubility $gMgI_2/100g\ Et_2O$
22.0	56.7
23.1	56.8
23.8	54.8
30.0	55.0

TABLE 5

ANALYSIS OF CRYSTALS OF MAGNESIUM IODIDE ETHERATE

Temperature °C	% MgI_2 (from I_2)	% MgI_2 (from Mg)	Moles ether/ mole MgI_2
0.0	45	45	4.6:1
15.0	59.5	55.7	2.8:1
15.0	-	56.6	3.0:1
20.0	60.5	61.2	2.5:1
20.0	68.4	64.3	1.9:1
22.8	65.5	68.9	1.8:1

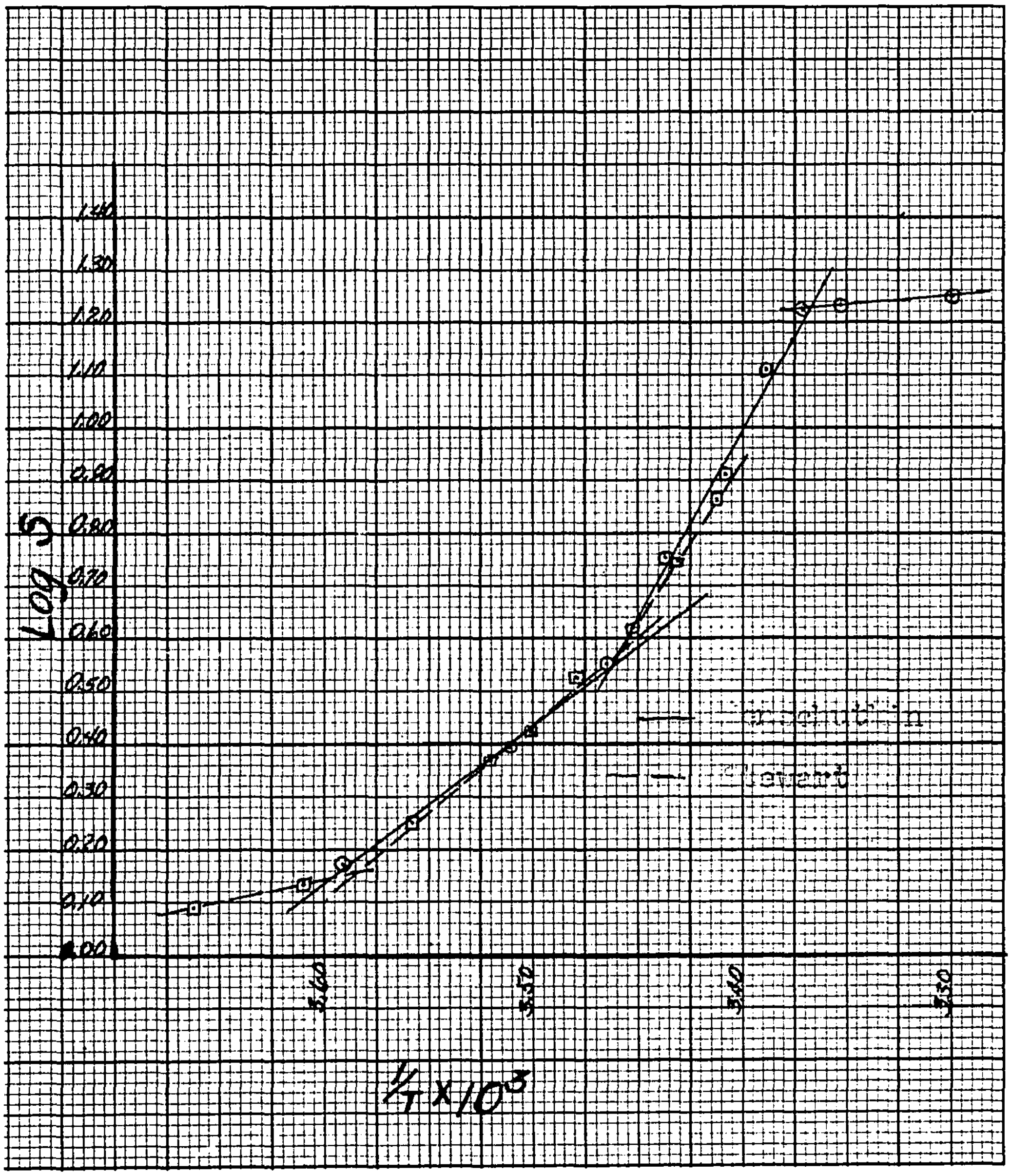
Several batches of magnesium iodide etherate crystals that were obtained at 0°C were evacuated at 25°C and about 20 millimeters until they reached an almost constant weight. If the loss of weight is considered to be ether, approximately three moles of ether were lost for each mole of magnesium iodide. Subsequent analysis of the residue showed that an additional mole of ether remained in the residue after this evacuation.

Since Menschutkin (1) and Stewart (8) had reported the solubility of magnesium iodide in ether and since the method of preparation of magnesium iodide in these experiments was different from theirs, it was thought advisable to compare the solubilities obtained by the three investigators. The data reported by Menschutkin and Stewart are recorded in Table 6. These data are compared with those recorded in Table 3 by plotting them in Figure 4.

TABLE 6

SOLUBILITY OF MAGNESIUM IODIDE IN ETHER

Temperature	Solubility in g $MgI_2/100gEt_2O$	
	Menschutkin	Stewart
0.0	-	1.23
4.0	-	1.37
5.4	1.49	-
8.0	-	1.78
11.0	-	2.30
11.8	2.48	-
12.6	-	2.65
14.4	-	3.33
15.6	3.58	-
16.6	-	4.19
18.1	5.72	-
18.5	-	5.52
20.0	-	7.27
20.4	8.15	-
22.2	12.8	-
23.6	16.8	-
25.0	17.2	-
30.0	18.2	-



Graph of Solubility of Magnesium Iodide

FIGURE 4

Magnesium Bromide

The results of the solubility determinations of magnesium bromide in ether are given in Table 7. The corresponding data obtained by Rowley (16) are also included for comparison. The solubility data obtained by Lewis are plotted in Figure 5. Comparison of these two sets of data is made by plotting the data in Figure 6.

The analysis of the crystals of magnesium bromide etherate at 0^{o}C indicated that the crystals contained three moles of ether for each mole of magnesium bromide as reported by Rowley (16).

Magnesium Chloride

The amount of magnesium chloride that dissolved in ether was so small that the analytical methods employed would not give results that were consistent. However, the results of the determinations made indicated that the solubility of magnesium chloride was less than 0.0001 mole per 100 grams of ether.

No indication, under these conditions, could be found for the existence of an etherate of magnesium chloride.

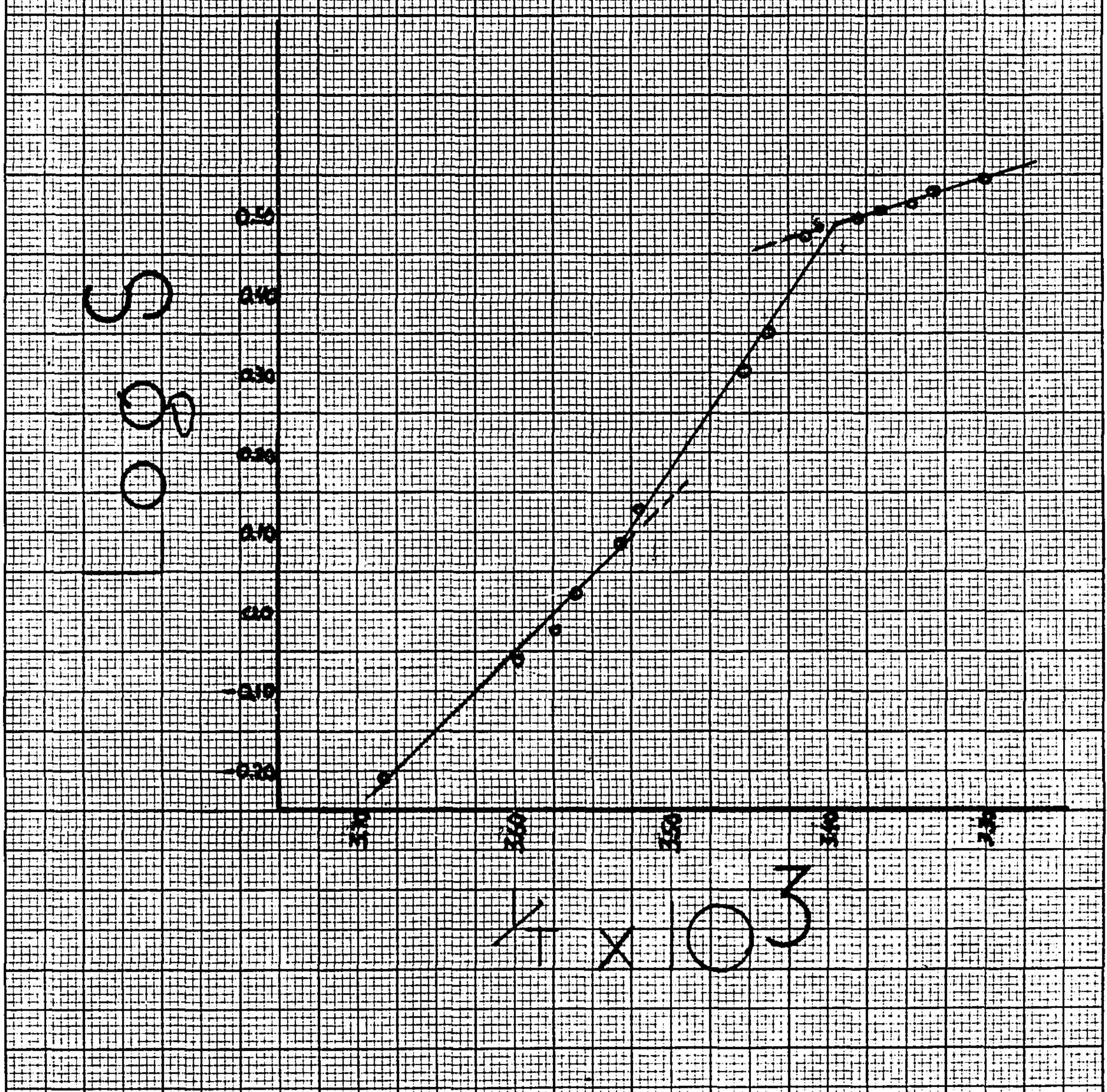
Magnesium Fluoride

Again, in the case of magnesium fluoride, as with magnesium chloride, the solubility was so small that

TABLE 7

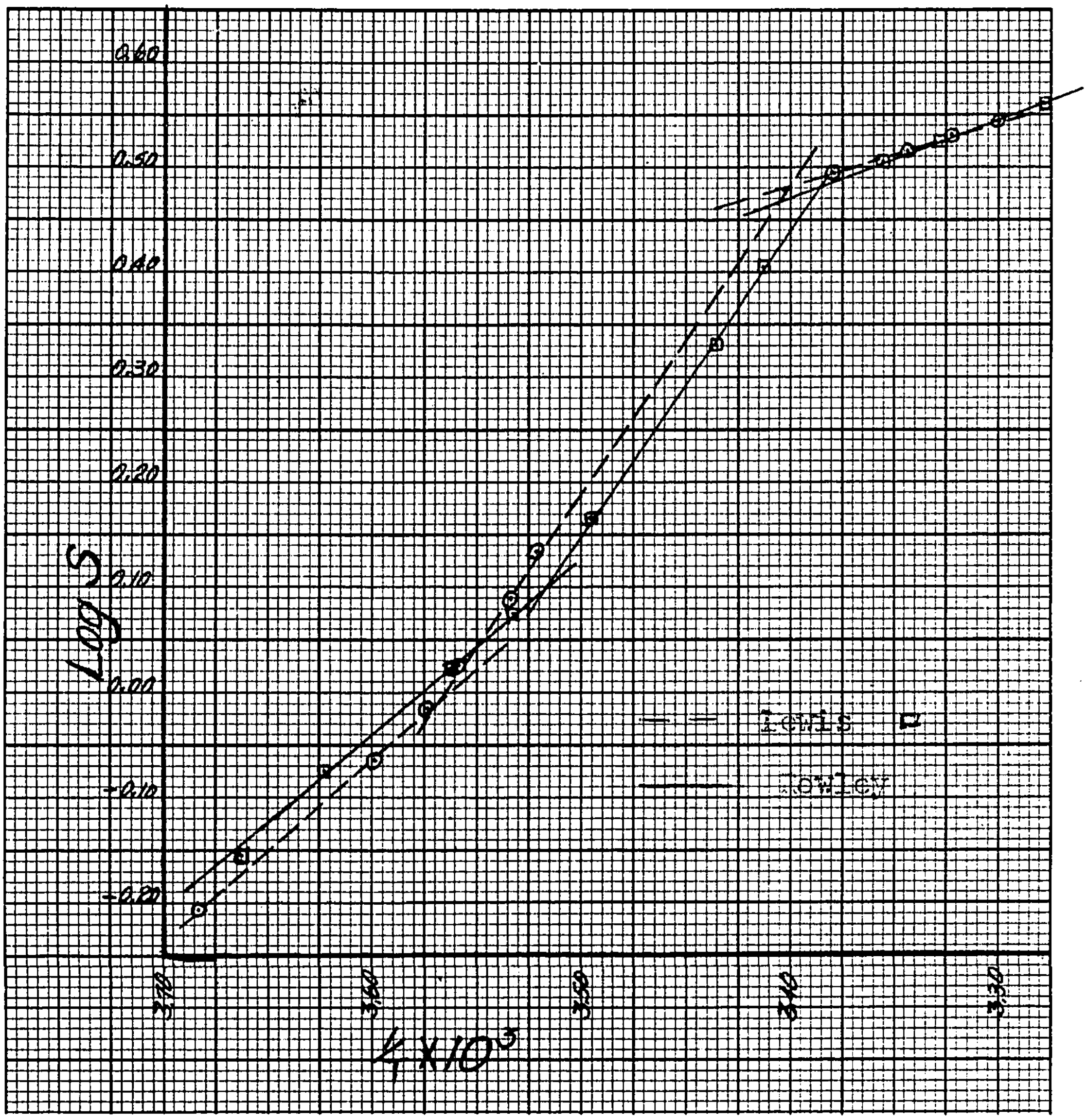
SOLUBILITY OF MAGNESIUM BROMIDE IN ETHER

Temperature	Solubility in g Mg Br_2/100g Et_2O	
	Lewis	Rowley
-1.5	0.62	-
0.0	-	0.10
3.0	-	0.84
5.0	0.87	-
6.8	0.97	-
7.8	-	1.05
8.0	1.06	-
10.0	1.23	-
10.1	-	1.19
11.0	1.35	-
13.0	-	1.47
18.0	-	2.14
20.0	-	2.53
	Equilibrium phase - Immiscible layer	
22.9	3.14	-
24.0	3.20	-
24.9	-	3.20
26.0	3.28	-
27.5	-	3.33
28.0	3.39	-
30.0	3.50	-
32.0	-	3.63



Graph of Solubility of Magnesium Bromide

FIGURE 5



Graph of Solubility of Magnesium Bromide

FIGURE 6

inconsistent results were obtained. However, the results obtained indicated that the solubility was less than 0.001 mole of magnesium fluoride per 100 grams of ether over the range of temperatures studies.

There could be no indication of the existence of a magnesium fluoride etherate of any definite composition. It was observed that upon evaporation of a large amount of ether solution of magnesium fluoride the residue was translucent just before being taken to dryness.

CHAPTER V

DISCUSSION

Solubility Relationships of Magnesium Halides

Many factors influence the solubility of chemical substances. It is known that a given substance may be quite soluble in one solvent while it is relatively insoluble in another. On the other hand, a given liquid may serve as a good solvent for certain types of materials and prove quite ineffective on other substances. A few statements will serve to review the relationship that exists between solvent and solute.

It is a well known axiom of chemistry that ionic compounds are more soluble in polar solvents than are covalent compounds. This dissolution results because the polar solvent molecules possess sufficient attraction for the ions of the solute to pull them out of their crystal lattice positions. At the same time the ions are solvated. Molecules which are incapable of these solution effects do not effectively dissolve ionic compounds.

It is evident that the nature of the solvent will affect the interaction between solute and solvent. This will be explored further later in this chapter. It is also true that variations in the nature of the solute itself are important. For the purposes of this discussion it should suffice to mention that in general, other factors being equal, solubility will increase with an increase in the size of the anion. This follows because with increase in the radius of the anion associated with a given cation, the force of attraction between the ions is decreased. As a result the solvent may more readily pull the ions apart--solution resulting.

As a rule, because of differences in the structure between inorganic and organic compounds, it would be expected that organic liquids should not be suitable solvents for inorganic substances unless these inorganic substances have some covalent character.

Water, because of its polar character, has the ability to dissolve materials of a wide variety. It is noted that the alcohols, although polar, possess less ability to dissolve ionic type compounds than does water and, as evidenced by their physical properties, are less polar than water. The ethers have a structure similar to that of both water and the alcohols, however, they are the least polar of the three types of compounds. The ethers thus show a reduced solvent action toward inorganic salts.

The use of ethyl ether as a solvent has a particular significance because of its widespread use in organic chemical synthesis. Its ability to dissolve many inorganic substances is recognized and this solvent power has been used in many organic reactions in which inorganic compounds have been employed as reagents or where they have been formed as by-products.

It is a general rule that the covalent character of a compound will increase with an increase in the size of the anion, other factors remaining the same. An application of this rule indicates that the tendency toward covalency of the magnesium halides should increase from magnesium fluoride to magnesium iodide. Some degree of evidence for this can be found by comparing the melting points of the substances.

From the above discussion it is not at all surprising to find that the solubility of magnesium iodide in ethyl ether was greater than that of the other halides. It would also be expected that the solubility of magnesium chloride and magnesium fluoride should be quite low. This has been found to be true.

There was some difficulty in obtaining consistent results in determining the solubility of both the magnesium chloride and magnesium fluoride. The methods of sampling and of determining the amount of inorganic salt present, were not of sufficient accuracy to match the low solubilities of the salts. The results obtained do indicate that there is a greater solubility in the case of magnesium fluoride than for magnesium chloride. It is known that, because of the extreme smallness of the ions, the elements of the second period have properties that are not in accord with the general properties of the other elements in that same family. It is possible that this might explain the reversal in the solubility trend from magnesium chloride to magnesium fluoride.

The solubility measurements made on magnesium iodide in this research are recorded in Table 3. These data were plotted in Figure 3. It was considered desirable to compare the solubility of magnesium iodide in ether as determined in this research with those made by Menschutkin (1) and stewart (8). The reported solubilities as reported by these investigators were tabulated in Table 6. These data were plotted in Figure 4. For comparison the solubility of magnesium iodide at 7 different temperatures was determined from the graphs in Figure 3 and Figure 4. These are listed in Table 8.

TABLE 8

COMPARISON OF MAGNESIUM IODIDE SOLUBILITY

Temperature °C	grams MgI_2 per 100 grams ether Lewis	 Menschutkin	 Stewart
0	2.80	-	1.23
5	3.45	1.38	1.38
10	4.53	2.14	2.10
15	6.53	3.25	3.39
20	10.6	6.49	7.27
25	17.4	17.2	-
30	18.8	18.2	-

Several observations can be made from the data in Table 8. In the first place there is general agreement in the 3 sets of data at the higher temperature. As a second observation it is obvious that the solubility measurements of both Menschutkin and Stewart are lower at the lower temperatures.

It should be recalled that the magnesium iodide used in this research was prepared by displacement. No free iodine was used. The magnesium iodide of the other researchers was prepared by direct union of the elements. it has been mentioned earlier in the paper that the presence of the free halogen in the ether will result in side reactions that will influence the nature of the product. Menschutkin and Stewart have both reported that their product was unstable and that it turned dark readily. They did not mention whether or not the color of the crystals was such as to indicate decomposition at the lower temperatures. In the present research the composition of the crystals used did not change from the time of preparation to the time of finishing the solubility measurements. This lack of decomposition was indicated by the fact that under the conditions of performing the experiment the color of the crystals and ether solution changed at most to a pale yellow.

Frequent comparisons of magnesium and iodide content indicated that the ratio Mg/I_2 and 1/2 throughout the experiment. Representative analyses are given in Table 9.

TABLE 9

RATIO OF MAGNESIUM TO HALIDE

Temperature °C	Ratio Mg/I_2	Ratio Mg/Br_2
22.8	1/1.90	
10.0 *	1/1.99	1/1.92
-1.5	1/1.99	1/1.96
0.0	1/1.97	1/2.00

* Upper layer. Other analyses made on crystals.

Rowley (16) had shown that the introduction of moisture after the preparation of magnesium bromide would increase the solubility. It was not felt that the introduction of moisture has been a factor in the increase in solubility of magnesium iodide for several reasons. If moisture had been introduced, certain irregularities would have shown up when the data were plotted. Instead, the graphs show consistency. Earlier experiments in getting this research organized showed that the introduction of moisture would result in the decomposition of the etherate and the appearance of free iodine. There would also be variation in the ratio of Mg/I_2. In all experiments, care was taken to exclude moisture from the solubility measurement tubes.

Table 4 of Chapter IV records some representative measurements of the ratio of magnesium iodide to ether in the lower oily layer that existed prior to the formation of crystals of magnesium iodide dietherate. These data indicate a small increase in magnesium iodide concentration as the temperature is reduced from 30°C to the point where the first crystals appeared. Frequent observations showed that over this same temperature range the volume of the upper layer increased at the expense of this lower, oily layer.

This is as would be expected. The lower layer would be a solution of ether in magnesium iodide. As the solubility of magnesium iodide in the upper layer decreases, a larger percentage of that substance should be found in the lower layer.

The solubility measurements of magnesium bromide in ether were made under the same conditions as those of magnesium iodide. It is noted upon referring to Figure 6 that the solubility of magnesium bromide in ethyl ether agrees closely with the solubility as reported by Rowley (17).

Formation of Etherates

Magnesium iodide and magnesium bromide. The graph in Figure 3 shows three discontinuities between the temperatures 30°C and 0°C. The break at 22.8°C represents the formation of a solid phase. Above this temperature the lower layer is the oily, immiscible layer. Table 5 shows the results of some analyses of the crystals at various temperatures. Because of the high vapor pressure of the etherate crystals it was difficult to obtain exact analysis of the composition of the crystals.

It is believed that the analyses do show a definite trend in the change in the number of moles of solvent per mole of solute as the temperature is reduced to 0°C.

The crystals formed at 22.8°C represent a formula of $MgI_2 \cdot 2(C_2H_5)_2O$. The dietherate is stable between this temperature and 17°C. From 17°C to 8°C the stable phase is the trietherate and between 8°C and 0°C the tetraetherate is the stable phase.

The greater solubility of magnesium iodide in ethyl ether would lead one to expect that etherates of magnesium iodide would be stable at higher temperatures than would the corresponding etherates of magnesium bromide. Rowley (15, 16, 17) had shown that at 0°C the stable etherate of magnesium bromide that was stable was the trietherate. He has obtained evidence from vapor pressure measurements (33) for the formation of $MgBr_2 \cdot 4(C_2H_5)_2O$ at a temperature of about -65°C.

<u>Magnesium chloride and magnesium fluoride</u>. No definite evidence could be obtained to suggest that either magnesium chloride or magnesium fluoride formed a compound

with ethyl ether. In the case of these magnesium halides the evidence is that they are more ionic and thus would have less tendency to dissolve and solvate in ether.

Preparation of Magnesium Fluoride

In Chapter II it was reported that attempts to prepare magnesium fluoride by methods reported in the literature had not met with much success. Table 1 gives data that indicate the instability of magnesium fluoride when heated and Table 2 indicates the effect of air upon the stability of magnesium fluoride.

It is known that the other magnesium halides are changed to magnesium oxide upon being heated in air. The weights obtained in the case of magnesium fluoride ignition are very close to those that would be obtained if oxygen had replaced the fluoride ion during the ignition.

Heats of Solution

The heat of solution of the different crystal phases in ethyl ether was calculated. The average differential heat of solution for magnesium iodide tetraetherate was found to be -6.7 kilocalories over the temperature range -1.5 to 8°. The average differential heat of solution for the magnesium iodide trietherate was found to be -11.7 kilocalories over the temperature range 8 to 17°, while the average differential heat of solution for the dietherate was found to be -19.1 kilocalories over the range 17 to 22.8°.

CHAPTER VI

SUMMARY

Magnesium iodide has been prepared by reacting magnesium with mercuric iodide in ether. The solubility of the resulting magnesium iodide has been measured between the temperatures 30°C and 0°C. From these solubility data evidence has been obtained to point to the existence of $MgI_2 \cdot 4(C_2H_5)_2O$ which is stable to 8°C; $MgI_2 \cdot 3(C_2H_5)_2O$ which is stable to 17°C; and $MgI_2 \cdot 2(C_2H_5)_2O$ which melts under ether at 22.8°C.

The solubility of magnesium iodide as prepared here is greater than that reported by Menschutkin and Stewart at temperatures wherein the equilibrium phase is solid.

Magnesium bromide has been prepared by reacting magnesium with mercuric bromide under ether. The solubility of the resulting magnesium bromide has been measured between the temperature 30°C and 0°. Agreement between these measurements and those of Rowley has been found.

Magnesium chloride was prepared and its solubility in ethyl ether was observed to be less than 0.0001 mole per 100 grams of ether.

An effort to prepare pure magnesium fluoride was made. This material was found to be unstable during the drying process. The solubility of the impure magnesium fluoride was determined and found to be less than 0.001 mole per 100 grams of ether.

No evidence for the existence of etherates of magnesium chloride or magnesium fluoride could be found.

The average heats of solution for $MgI_2 \cdot 4(C_2H_5)_2O$ was found to be -6.7 kilocalories over the temperature range -1.5 to 8°. For $MgI_2 \cdot 3(C_2H_5)_2O$ the value was -11.7 kilocalories over the temperature range 8° to 17°. $MgI_2 \cdot 2(C_2H_5)_2O$ had an average heat of solution of -19.1 kilocalories over the temperature range 17° to 22.8°.

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